better understanding of the electronic behaviour of the metal centre, obtainable from the detailed knowledge of its coordination environment.

In our presentation, we will report several structural studies, carried out by conventional X-ray diffraction methods, of *classical or non-classical hydride* complexes, and of mixed hydride-dihydrogen compounds in which the central metals are transition metal atoms. We will discuss different approaches applied to reach plausible spatial assignments for these extra-light-atoms and to carry out their conventional free-atom refinement. Our experience indicates that special effort should be dedicated to the precise localization of the atom positions, as their subsequent refinement has been observed to be very sensitive to this step.

The molecular parameters obtained are compared with reliable data from neutron diffraction analysis of related complexes. The validity of the determinated molecular parameters have been checked against several external or indirect informations: extended Hückel calculations have been used to inspect the coplanarity of hydrides with the metal in $RuH(\eta^2-H_2)I(PCy_3)_2$, or NMR dipole-dipole spin-lattice relaxation times (T_1) have been measured to estimate interatomic H-H distances in $[OsCl_2(\eta^2-H_2)(PzH)(PiPr_3)_2]$, $[OsCl(\eta^2-H_2)(biim)(PiPr_3)_2]Cl$, and $[OsH_3(\eta^2-PyS)(PiPr_3)_2]$. Examples reported will include complexes of different nuclearities, with metals from the second and third rows.

MS-07.01.04 DESIGNING MULTI-DIMENSIONAL HOST STRUCTURES OF CYANOMETALLATE SYSTEMS; STATIC AND DYNAMIC BEHAVIOUR OF GUEST MOLECULES IN CRYSTAL. By T. Iwamoto, Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Japan.

The ambidentate character of cyanide anion, CN^-, is favourable for designing various multi-dimensional structures with appropriate coordination centres. Possible building blocks are cyanometallates $M(CN)n$ of octahedral (n=6), trigonal-bipyramidal (5), tetrahedral (4), square planar (4) and linear (2) configurations to extend 3D frameworks, 2D networks, or 1D chains with other joining coordination centres and/or complementary ligands modifying and/or reinforcing the cyano-linked multi-dimensional structures. Structural varieties with the topologies such as single and double 3D frameworks, single and interwoven 2D layers, bent and straight 1D chains, 1D honeycomb channels, have been materialised for the systems involved with such cyanometallate moieties as $Ni(CN)4$, $Cd(CN)2$, $Cd(CN)4$, $Hg(CN)4$, $MCd(CN)4$ (M=Cu,Hg,Zn), $Cd2(CN)7$, $Cd3(CN)8$, $Ag(CN)2$, $Ag2(CN)3$, etc. The inclusion compounds are formed by accommodating various kinds of guest molecules in the cage, interlayer, intralayer, intermesh, channel and interchain cavities with definite crystal structures. Some of them mimic the mineral structures of cristobalite, pyrite, clay, zeolite, etc. Single crystal X-ray diffraction is essential to ascertain the static inclusion structures, some of which are accompanied with orientational disorder of not only the guest but also the linking cyanide. Solid state NMR supplies information advantageous to understanding disorder and dynamic behaviour of the hosts and guests. The structural features of these inclusion compounds are reviewd comprehensively, in particular on the developements in Australia, Canada, Japan and other territories.

MS-07.01.05 SYMMETRY AND MOLECULAR RECOGNITION IN CLATHRATES. G. Tsoucaris and G. Le Bas, CNRS UPR180, Univ. Paris XI, Chatenay-Malabry, France.

Symmetry considerations are particularly important in the organisation of clathrates. First, a distinction should be made between **lattice clathrates** and **intramolecular clathrates**. In the former, the cavities are created within the crystal as large intermolecular voids between several host molecules. In the latter, the host molecule already comprises an intramolecular cavity and is capable of inclusion in solution.

In general, **crystal symmetry elements** play a most important role in the organisation of the cavities. In lattice clathrates, a channel is often generated by a crystallographic helical axis. A classical example is the urea clathrate where a 6_1 axis relates urea molecules linked together by H-bonds, in a way that leaves a channel around the helical axis. Recent work on the diol clathrate family has shown a similar role of a 3_1 axis; moreover, the diol host molecules are located at a crystallographic 2 axis (Bishop, Inclusion compounds, 1991, Vol.5, 1). As intramolecular clathrates, cyclodextrins (cd) involve several types of crystallographic rotation axes, of order 2,3,4,6. In the usual β-cd clathrates, a two-fold axis relates two host molecules within a dimer. Here this symmetry element plays a significant stereochemical role, by creating an intradimer cavity which considerably enlarges the intramolecular cavity of β-cd. With

the clathrate α-cd.cyclopentanone (Le Bas, 1985, Thèse de Doctorat d'Etat) we have the exceptional case in molecular clathrates where a high order molecular symmetry element (6-fold axis) coincides with the same crystallographic element.

Certain hosts forming intramolecular clathrates exhibit high **non crystallographic symmetry**. This is the origin of problems related to pseudosymmetry and disorder. In some cases the non crystallograpic symmetry is nearly perfect (anion cryptates, Dietrich et al, Helv. Chim. Acta, 1984, 67, 91). For β-cd's the 7-fold host axis often generates severe disorder of the guest. A relevant problem pertains to the criteria indicating that the refinement of the disordered molecule is carried out to the end with the given data.

An important aspect in modern molecular science is the question of **molecular recognition**. Clathrates provide examples where the host/guest recognition is based upon crystal symmetry. Thus in the complex γ-cd .12-crown-4 (Kamitori, J.A.C.S.,1987,109,2409) the coincidence of the host and guest crystallographic symmetry (four-fold axis) governs the clathrate formation.

Chirality and enantiomeric discrimination is a particular case of molecular recognition. Two examples illustrate the distinction between **intramolecular dissymmetry of the host and dissymmetry** arising mainly from the the crystal environment. In the case of the included compound 1,7-dioxaspiro (5,5) undecane 1 (Rysanek et al, Acta Cryst., 1992, C48, 1466), this volatile pheromon has been introduced in a dissymmetricaly modified cyclodextrin where two out of the seven glucosidic units are substituted differently from all others. Combination of the above lack of 7-fold symmetry with the classical glucose dissymmetry results in a total enantiomeric discrimination of the racemic guest. This last molecule is located exactly in the center of the host cavity. We have here an example of chiral influence within a dissymmetric intramolecular cavity. We mention that in the natural β-cd with 7-fold symmetry the same pheromon exhibits severe disorder associated with lack of chiral discrimination.

The influence of crystal environment dissymmetry will be illustrated with an example of asymmetric synthesis which occurs within a native β-cd clathrate. Phenyl ethyl malonic acid undergoes thermal decarboxylation at 100°C leading to an enantiomerically enriched product (Arad-Yellin et al, Weizmann Institute, personnal communication). Crystal structure determination has shown a different microenvironment of the two carboxylic groups; this is considered as the origin of the asymmetric synthesis.